1 Miniaturized Spectrometers

1.1 General Set-up

The classical spectrometer consists of an input slit, a rotating dispersive element (prism or grating), an output slit and a single detector. This arrangement allows the separation of polychromatic radiation into its spectral components. The main advantages are the high sensitivity and the low stray light. Several drawbacks, such as the non-parallel measurement, the moveable elements and the space consuming dimensions, were overcome by the development of array spectrometers. This kind of spectrometer uses a detector array instead of a single detector and therefore only needs fixed components. Meanwhile, they are widely used in PC coupled, stand-alone as well as hand held devices and begin to find their applications even in the online process measurement.

1.1.1 Gratings

Most time gratings are used as the dispersive element in array spectrometers. They have the advantages of higher dispersion and lower production costs than prisms. The basic grating equation is as follows:

$$\sin\Theta_m = \sin\Theta_i + m\frac{\lambda}{d} \tag{1}$$

with θ_i and θ_m - angles of the incident as well as the diffracted wave directions to the normal of the grating surface, λ - wavelength, d - grating period and m - order of diffraction (integer value, $m = 0, \pm 1, \pm 2, ...$). This equation is valid for reflexion gratings, whose grooves are perpendicular to the plane of incidence. Gratings in spectrometers are more often than not used in reflectance mode.

The equation shows, that for $m \neq 0$ the radiation of different wavelengths will be separated angularly. This effect is called dispersion. Furthermore, each wavelength is diffracted into different discrete angles according to the order m, causing an ambiguity. Spectrometers usually use the dispersed light of one order. Influences of other orders and the non-dispersive zeroth order have to be suppressed. Fig. 1 shows the angular separation for monochromatic and polychromatic radiation, caused by a grating.

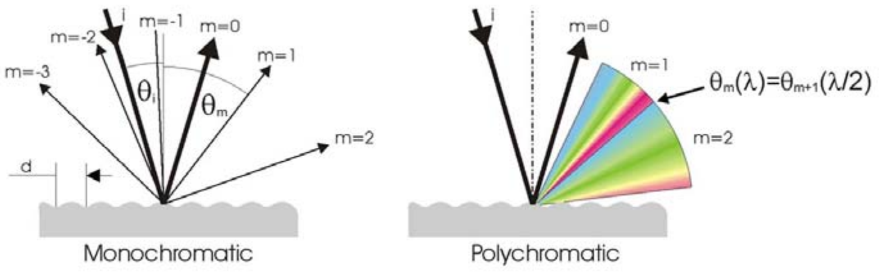


Fig. 1 Angular separation of mono and polychromatic radiation

It demonstrates the overlap between the different orders - the diffraction angle for m = 1 in the red region coincidences with the corresponding angle of half of the wavelength for m = 2. The free spectral range (range without overlap) becomes smaller for higher diffraction orders.

As mentioned above, the order of diffraction can have negative or positive values. The common convention, also used here, calls the order positive, if the angle of diffraction exceeds the angle of incidence and lies on the opposite side of the grating normal.

The grating equation determines the angles of diffraction, but gives no information about the intensity distribution into the different orders. The fraction of light intensity diffracted in one order, related to the entire incident intensity is called diffraction efficiency of this order. Symmetric profiles as the sinusoidal shape of the gratings in fig. 1 are not very effective. The efficiency can be tuned by varying the shape and depths of the grooves. An increased efficiency is obtained by a saw tooth profile. The angle of the swots has to satisfy the condition of the regular reflexion law to reflect the incident beam into the angle of the chosen diffraction order. This is called blazing and the condition can be met exactly for one wavelength only, the blaze wavelength. It is practical to shift this wavelength in the region, where the other components of the system have low effectivity, e.g. the light source or the detector, to achieve a homogenisation of the system's performance.

The change of diffraction angle corresponding to a small change in wavelength is called angular dispersion of a grating. The following equation is obtained by differentiating the grating equation to the wavelength with fixed angle of incidence:

$$\frac{d\Theta_m}{d\lambda} = \frac{m}{d \cdot \cos\Theta_m} \qquad (2)$$

The linear dispersion dl/dλ is the product of the exit focal length f of the spectrometer and its angular dispersion:

$$\frac{dl}{d\lambda} = f \cdot \frac{d\Theta_m}{d\lambda} = \frac{f \cdot m}{d \cdot \cos\Theta_m} \qquad (3)$$

It defines the extend of the spectrum on the detector array.

1.1.2 Spectrometer Set-up

Array spectrometers consist of an input slit, a grating, possibly other optical imaging elements, a line detector and a stable housing. Several standard optical arrangements are used for spectrometers. The basic demand for the design is to use collimated light for the dispersion - this improves the measurement accuracy. One can distinguish between plane grating set-ups and concave grating spectrometers. The latter type combines diffraction and imaging in one element. If plane gratings are applied, it is necessary to use additional optical elements for beam shaping, preferably spherical or aspherical mirrors for ray collimation and focusing.

The following figures show examples for both types of set-up (so-called mounts).

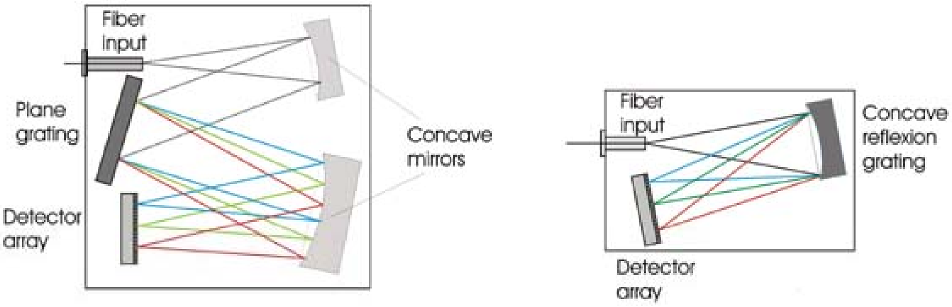


Fig. 2 Schemes of Czerny-Turner and flat field concave grating spectrograph

The advantage besides the lack of moving parts is the quasi-parallel measurement of the whole spectrum, which reduces the measuring time. Further advantages are the robustness and the small dimensions. The flat field arrangement is further advantageous because of fewer optical elements, which have to be adjusted. This type of grating offers a plane focal line, which can be detected by the plane detector array without remarkable focusing errors.

Nevertheless, plane grating spectrometers as the Czerny-Turner show improved optical properties because of better compensation possibilities of imaging errors. Usually, the most efficient diffraction order of the grating is detected by the array; the detection of other orders is avoided by design or suppressed by several means (filters, ray traps).

One has to say, that array spectrometers show some disadvantages, too: The integral illumination over the full wavelength range increases the stray light, compared with monochromatic set-ups. Furthermore, the sensitivity is lower than of a monochromator, which can even be fitted out with a photo multiplier. The precision and resolution is normally less than that of laboratory instruments with a turnable dispersive element.

The first array spectrometers included original gratings, manufactured by holography (interference of a splitted laser beam) or mechanical ruling. Holographic gratings show less stray light because of their better surface quality than those of mechanically proceeded ones. Furthermore, it is possible to produce holographic gratings with reduced imaging errors by a special design of the exposure arrangement.

Such master gratings are replicated into epoxy layers (with an aluminium reflexion layer and a protection coating) to reduce the costs of the spectrometer. A further price reduction is obtained with a replication of the master gratings by injection moulding into a plastics material, e.g. PMMA. This technique is useable for less demanding applications because of a deterioration of the optical properties.

The radiation inside the spectrometer commonly propagates in free space (air or glass). The Zeiss spectrometer MMS is an example for this design.

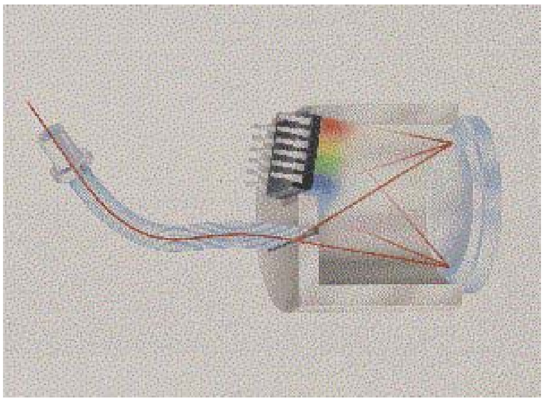


Fig. 3 Free space spectrometer MMS UV (Carl Zeiss Jena)

Another kind of spectrometer is based on the propagation in a slab wave guide (the LIGA spectrometer). The solution offers the possibility of an extreme miniaturization. This spectrometer, manufactured by Boehringer Ingelheim microParts GmbH (Germany), is shown in the following figure.

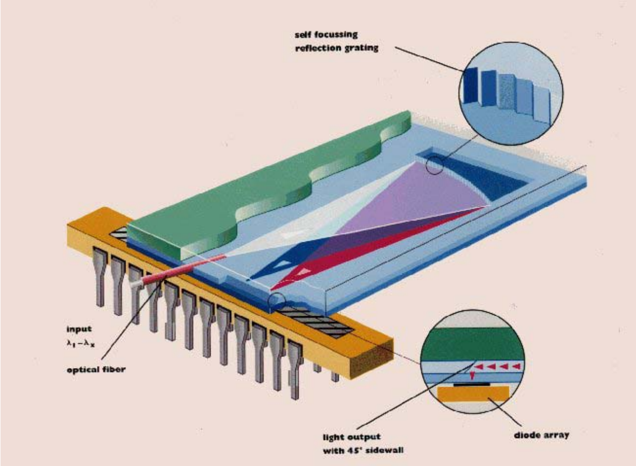


Fig. 4 Waveguide VIS spectrometer (Boehringer Ingelheim microParts Dortmund)

Modern array spectrometers are often fitted out with a fiber optic input for a more convenient adaption to the measuring situation. There are used single/ multimode fibers with or without an additional slit or fiber bundles designed as cross section transformer from cylindrical to rectangular (slit) shape.
The detectors used in UV/VIS spectrometers are silicon-based CCD or photodiode arrays. CCD arrays show a higher sensitivity, but diode arrays offer a much better dynamics. The proper selection of the detector array for a special application can improve the performance of the whole system or can just make it possible. Further information about the mode of operation and the application oriented selection of detector arrays can be obtained from chapter 2 of these basics (Line Arrays for Miniaturized Spectrometers).

1.2 Spectrometer Parameters

1.2.1 Wavelength Range

Array spectrometers are available for wavelengths from the UV (200 nm) and VIS to IR (...3 µm). Wavelength ranges of commercial array spectrometers are indicated in the following figure:

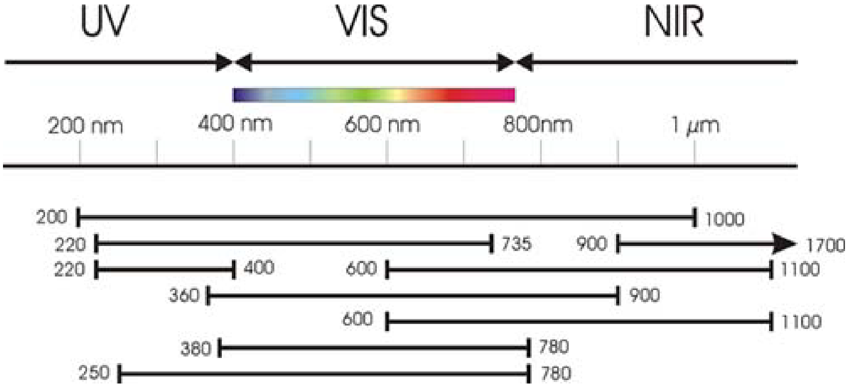


Fig. 5 Scheme of partial electromagnetic spectrum and of wavelength ranges of commercial spectrometers

The size of the spectrometer is determined by the wavelength range in connection with the desired optical resolution (see below), demanding in a certain focal length. JETI´s series of specbos instruments currently covers the range of 380 ... 760 nm, specbos 1001 UV 240 ... 480 nm and the JETI spectraval series measures between 350 and 850 nm.

1.2.2 Resolution

Several definitions are used for the resolution of a spectrometer. One has to distinguish clearly between the optical or spectral and the digital or pixel resolution.

The **optical resolution** $\Delta\lambda$ is defined by the wavelength difference of two peaks close together in one spectrum and of same intensity, which can be separated. The dip between the peaks has to reach a minimum of at least 19 %, related to the maximum intensity. This definition is called the Rayleigh criterion.

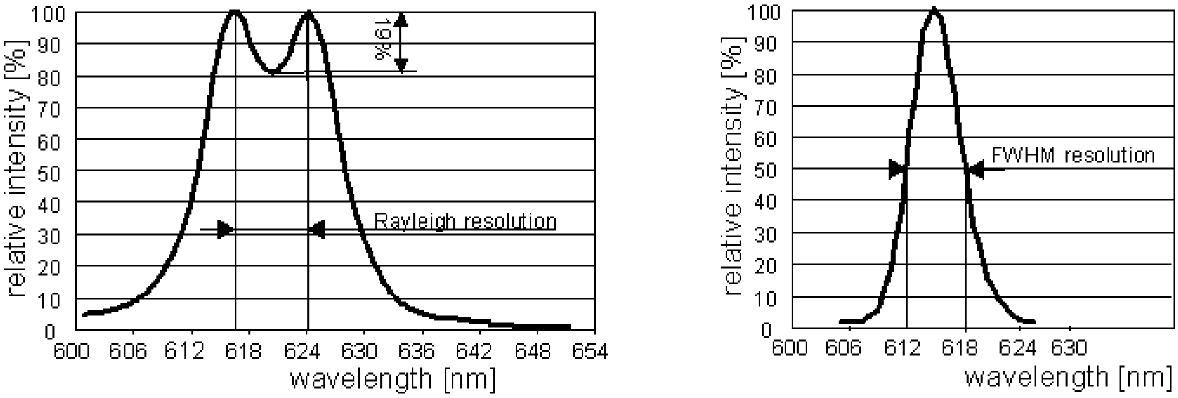


Fig. 6 Definition of the optical resolution (Rayleigh and FWHM)

Another more practical definition is related to the measured width of a narrow spectral line. Its measured bandwidth $\Delta\lambda_{FWHM}$ (FWHM – full with at half maximum) gives information about the broadening of the line. This bandwith amounts to about 4/5 of the resolution according to the Rayleigh criterion.

The optical resolution is determined by the width of the input slit, the focal length of the optical system and the dispersion of the grating. $\Delta\lambda_{FWHM}$ is inversely proportional to the linear dispersion dl/dλ and directly proportional to the output slit width w´:

$$\Delta\lambda = w' \cdot \frac{d\lambda}{dl} \qquad (4)$$

This equation can easily be used for the estimation of a spectrometer resolution, especially with 1:1 imaging, where the width of the input slit equals to the width of the output slit (w = w´). The smaller the slit width, the higher is the resolution. However, reduced slit width reduces the optical energy, entering the spectrometer, too. This can cause sensitivity problems for a spectrometric system. Common resolution values of miniaturized VIS spectrometers lie in the region of 2 .. 12 nm, values even below 1 nm are possible. The core diameter of the input fiber influences the optical resolution, if it acts as the input slit.

A separate parameter is the **pixel or digital resolution**. This is the spectral bandwidth, which is detected by one pixel of the array and is determined by the width of the pixel and the dispersion of the spectrum. Common values are 0.4 ... 5 nm/pixel. JETI spectrometers are available with 0.6 to 4 nm/pixel. The digital resolution is related to the spectral resolution via the imaging properties of the spectrometer.

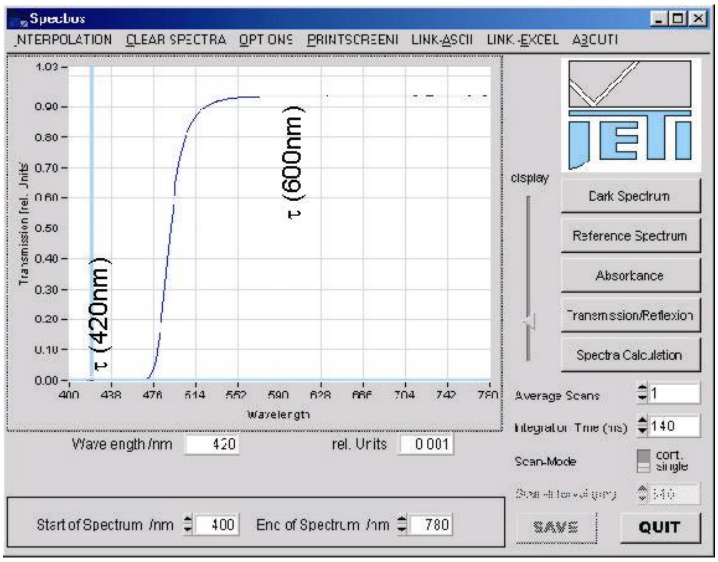
The ratio of digital to spectral resolution should be ≥ 3 to detect precisely a peak in the spectrum (rule of thumb).

1.2.3 Stray Light

Stray light is radiation of false wavelengths, which strikes a pixel of the detector array. It is caused by imperfections of the grating, dust, reflexion of non-used orders at the spectrometer housing or errors of the other optical elements. This parameter influences the precision of a spectroscopic measuring system in a crucial way. It gets measured by a broadband illumination of the input slit through a color filter with long pass characteristics. The Schott glass GG 495 is a filter commonly used therefore. The stray light S is the ratio of the transmission in the blocked wavelength region below the filter edge e.g. at 420nm (τ(420 nm)) to the transmission in the non-blocked region e.g. at 600nm (τ(600 nm)).

$$S[\%] = 100\% \cdot \frac{\tau(420nm)}{\tau(600nm)} \qquad (5)$$

It shows the influence of the light of longer wavelengths, passing the filter, on the unwanted intensity in the blocked region. A measured spectrum is shown in the following figure.



Wavelength /nm 420
rel. Units 0.001
Average Scans 1
Integration Time (ms) 140
Scan-Mode
Start of Spectrum /nm 400
End of Spectrum /nm 780

Fig. 7 Measurement of stray light

In case of a low stray light level (as in fig. 7) an additional neutral density filter is used for the measurement in the non-blocked region, which will be removed for the measurement in the blocked region.

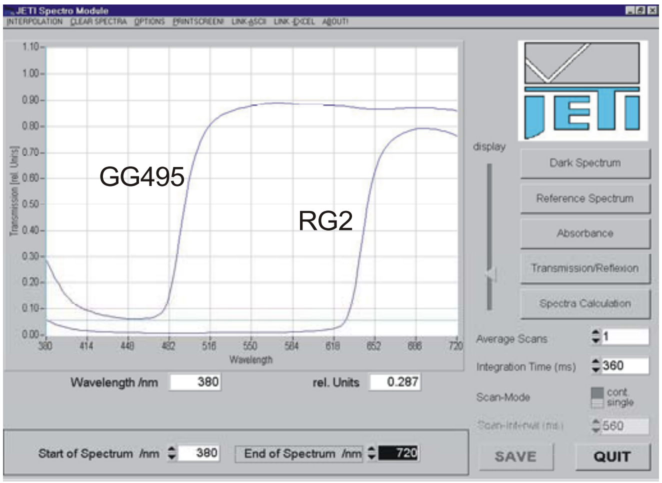
$$SL[\%] = 100\% \cdot \frac{\tau(420nm) \cdot \tau(NDfilter)}{\tau(600nm)} \tag{6}$$

A standard measurement method is described in the ASTM standard test method E 387 (available from www.astm.org). Detailed information about modifications of the measurement procedure and their influence on the result can be obtained from the Agilent technical note "Measuring the stray light performance of UV-visible spectrophotometers" (available at: www.chem.agilent.com/scripts/Literature Search. asp).

Another often applied stray light measuring method uses a monochromatic light source (e.g. a HeNe laser). The intensities at the laser wavelength and at another wavelength, several 10 nm away from the laser wavelength are measured. The ratio of the latter to the former is a measure for the stray light of the system. This measuring method provides much better values, but is more distant to the main practical applications, where a broadband illumination is used. Therefore, the method, described first, is recommended.

The stray light causes a non-linearity of the signal at lower power levels and thus limits the measuring range of the system. For example: the signal in the blue region of a VIS spectrometer depends on the incident intensity in the other regions of the spectrum. This effect cannot be compensated precisely by mathematical calculations in the software.

Every specification of stray light has to be given in connection with the used measuring conditions. One has to keep in mind, that the higher the bandwidth of the light entering the spectrometer, the higher the measured stray light ratio. The value, measured with a long pass filter with an edge in the red region of the spectrum is not comparable with a value, measured with a yellow edge filter (see the following figure).



Wavelength /nm 380
rel. Units 0.287
Average Scans 1
Integration Time (ms) 360
Scan-Mode
Scan-Interval (ms) 560
Start of Spectrum /nm 380
End of Spectrum /nm 720

Fig. 8 Stray light measurements with GG 495 and RG 2

The stray light of array spectrometers is mainly higher than of monochromators due to the lack of an output slit.

1.2.4 ADC Resolution

The analog intensity distribution of the optical spectrum on the detector array has to be converted pixelwise to a digital signal by an analog digital converter (ADC). Common electronic resolutions are 12 ... 16 bit (4095 ... 65 535 counts full scale). These numbers are finally reduced by the dark spectrum of the line array and the driving of the converter. The ADC resolution should be in a suitable ratio to the stray light of the spectrometer and to the dynamics of the detector array. The dynamics D of the entire system is determined by the ADC resolution R_{ADC}, divided by the noise signal Φ.

$$D = \frac{R_{ADC}}{\Phi} \tag{7}$$

A 12 bit spectrometer with a noise signal of 4 counts offers a dynamics of about 1000.

1.2.5 Integration Time

The light intensity coupled into a spectrometer and illuminating a pixel, results in a proportional signal from the AD converter. The exposure time of the light to the pixel is called integration time and is a main parameter to adjust the ADC signal. A level between 2/3 and full scale is suited for best measuring results, using the full dynamics of the system. Off scale peaks or regions in the spectrum have to be avoided. Common values for the integration time of array spectrometers are 20 ... 5000 ms. Several instruments, as the JETI spectroradiometer, specbos 1201, spectraval CAM and spectraval VIS, are equipped with an automatic integration time adaption.

1.2.6 Spectral sensitivity

The sensitivity of a spectroscopic system E(λ) is another important issue in many applications, especially in fluorescence detection, and is a main criterion for the choice of a spectrometer. It is measured in counts/ Ws and means the ADC signal r [counts] divided by the optical energy P (λ) · t_{int} [Ws], entering the spectrometer optical input.

$$E(\lambda) = \frac{r}{P(\lambda) \cdot t_{\text{int}}} \qquad (8)$$

The spectral sensitivity has to be specified for a given wavelength mainly because of the spectral dependencies of the grating efficiency and the detector sensitivity. The measurement can be done with bandpass filtered white light illumination or a monochromator, from which the radiant flux P (λ) is known.

Of course, sensitivity data have to be related to the ADC resolution of the read out electronics. The main uncertainity in sensitivity measurements is caused by the measuring error of P (λ), coupled into the spectrometer.

The spectral sensitivity can be adapted in certain limits to the application by a proper selection of the spectrometer’s detector array (see chapter 2 "Line Arrays for Miniaturized Spectrometers").

1.2.7 Wavelength and Intensity Calibration

The AD converter delivers the spectral signal in counts for each pixel of the line array. The pixels are numbered and these numbers have to be transformed into the corresponding wavelength. This can be done by a multiorder polynom as follows:

$$\lambda(n) = k_0 + k_1 \cdot n + k_2 \cdot n^2 + k_3 \cdot n^3 + \ldots + k_i \cdot n^i \qquad (9)$$

where n is the pixel number, k_0 [nm] the wavelength of the first pixel, k_1 [nm/pixel] the pixel resolution and k_2, k_3, .., k_i are the higher order coefficients.

This approximation with a polynom gives a wavelength precision, which has to be taken into consideration in the application. The choice for the order of the polynom depends on the non-linear behaviour of the spectrometer. The linear approximation is sufficient for a LIGA Spectrometer, whereas a higher order polynom is necessary for the Zeiss MMS.

The calibration can be done by relating the peaks of a suited spectral lamp (e.g. Hg in the VIS range) to the corresponding pixel and subsequent calculation of the k-parameters by regression (e.g. in Excel). JETI offers a special fit program for this purpose. This program can be used to measure the spectra, indicate the peaks, calculate the k-parameters and check the result. A spline fit is used to get a subpixel precision.

A easy way to check the calibration of a spectrometer for somebody who has no special spectral lamp is to use a common fluorescent lamp (F11, possibly on top of the lab), which has a spectrum as shown in the following diagram. The intense peaks of 546 and 614 nm can be used for a roughly test of the calibration.

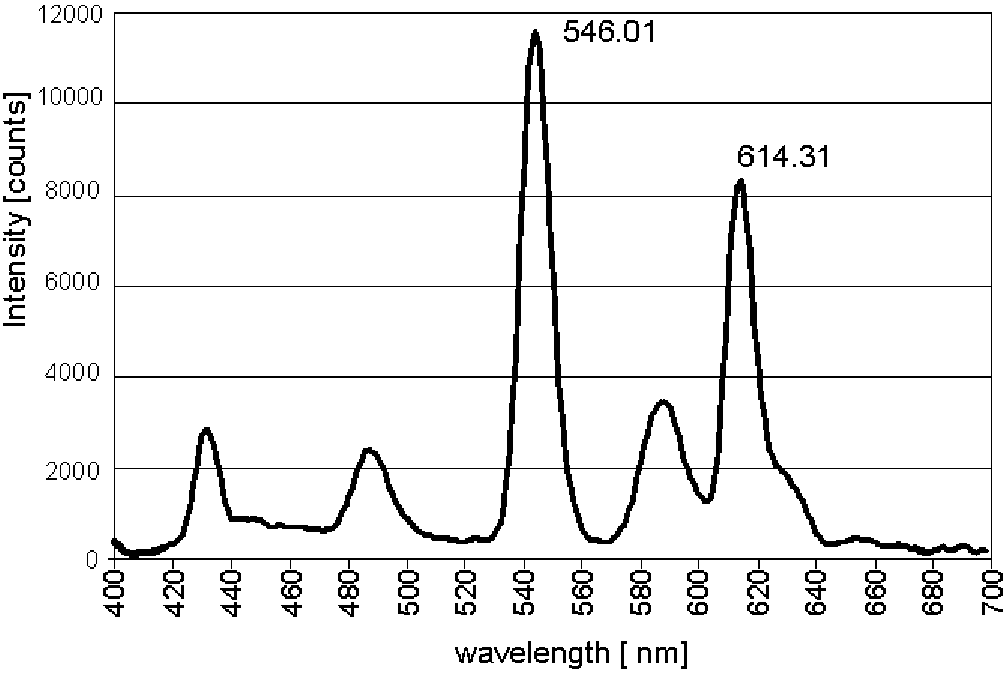


Fig. 9 Typical spectrum of a F11 (TL 84) lamp

Something else, sometimes mixed with the wavelength calibration, is the calibration of the intensity axis. A non-calibrated spectrometer as the JETI specbos 1001 has an intensity axis (y- axis) in counts or percent. Therefore, only relative measurements of light sources, e.g. the spectral distribution of LED, are possible. One has to keep in mind, that the obtained spectrum is weighted with the instrument function (grating efficiency, transmittance, detector sensitivity). Spectrometers with calibrated intensity axis are called spectroradiometers (see chapter 3.4).